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Sulfur analogs of fluorinated pyrones, chromones and coumarins

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REVIEW

Sulfur analogs of fluorinated pyrones, chromones and coumarins

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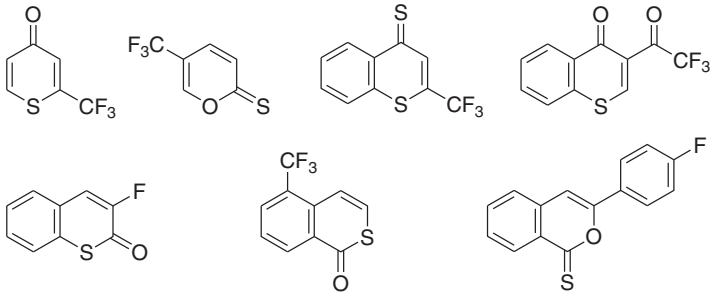
This mini-review describes the synthesis and reactions of sulfur analogs of partially fluorinated pyrones, chromones, coumarins and isocoumarins and their utility as building blocks for the synthesis of trifluoromethyl-containing heterocyclic compounds with biological interest.



Keywords: sulfur analogs of pyrones, chromones, coumarins and isocoumarins; fluorine-containing heterocycles

1. Introduction

Published data on the synthesis and reactivity of sulfur analogs of fluorinated α- and γ-pyrones, chromones, coumarins and isocoumarins are summarized. The main attention is paid to the polyfluoroalkylated derivatives of these sulfur-containing six-membered heterocycles. Their partially hydrogenated derivatives are not discussed. The literature data clearly indicate that, although these heterocycles are less reactive than the corresponding oxygen-containing analogs, they are rather susceptible to nucleophilic attack and some of them are attractive building blocks for the synthesis of various heterocyclic compounds containing the R^F group.

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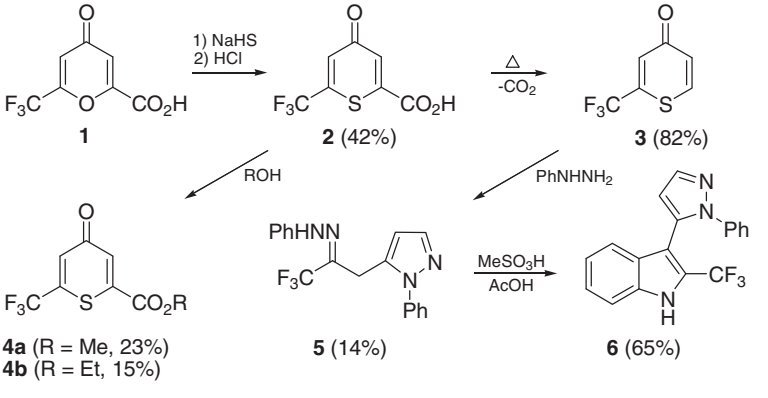
2. Sulfur analogs of fluorinated γ- and α-pyrones

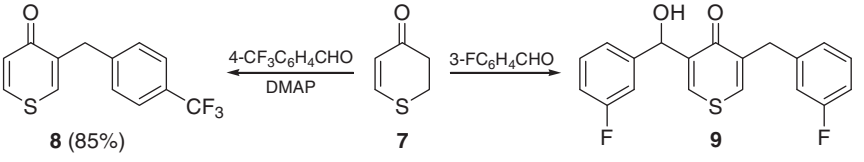
While trifluoromethylated α- and γ-pyrones have been extensively investigated regarding their synthesis and chemical properties (*1–6*), little attention has been paid toward the reactivity of their sulfur analogs, probably owing to the lack of general methods for the preparation of these compounds. Only a handful of papers describing some fluorine-containing thiopyrones are present in the literature.

It was found that treatment of 6-(trifluoromethyl)comanic acid **1** with sodium hydrogensulfide afforded 4-oxo-6-(trifluoromethyl)-4*H*-thiopyran-2-carboxylic acid or 6-(trifluoromethyl)thiocomanic acid **2**. When heated or treated with H_2SO_4, this acid easily underwent decarboxylation leading to 2-(trifluoromethyl)-4*H*-thiopyran-4-one **3**. As a result, both methyl and ethyl 6-(trifluoromethyl)thiocomanates **4** were obtained in low yields (*7*). The reaction of thiopyrone **3** with phenylhydrazine led to the formation pyrazole **5**, which upon heating in $MeSO_3H$/AcOH gave 3-(1-phenylpyrazol-5-yl)-2-(trifluoromethyl)indole **6** in good yield (*8*) (Scheme 1). Note that the latter products were also obtained from 2-(trifluoromethyl)-4*H*-pyran-4-one (*8*).



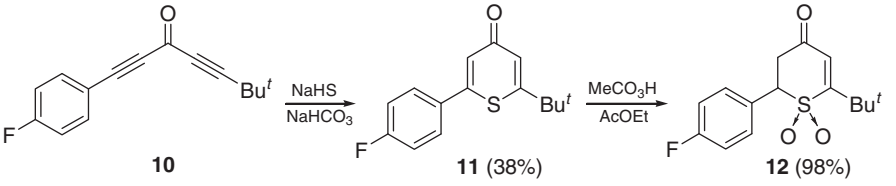
Scheme 1. Synthesis and reactivity of 6-(trifluoromethyl)thiocomanic acid **2**.

Condensation of 2*H*-thiopyran-4(3*H*)-one **7** with 4-(trifluoromethyl)benzaldehyde in the presence of 4-dimethylaminopyridine (DMAP) at room temperature for 4 h via domino aldol-rearrangement reactions gave 3-substituted thiopyran-4-one **8** in 85% yield. At higher temperature, 3-(3-fluorobenzyl)-5-[(3-fluorophenyl)hydroxymethyl]-4*H*-thiopyran-4-one **9** was identified as the aldol condensation–Baylis–Hillman adduct in the reaction with 3-fluorobenzaldehyde (*9*) (Scheme 2).



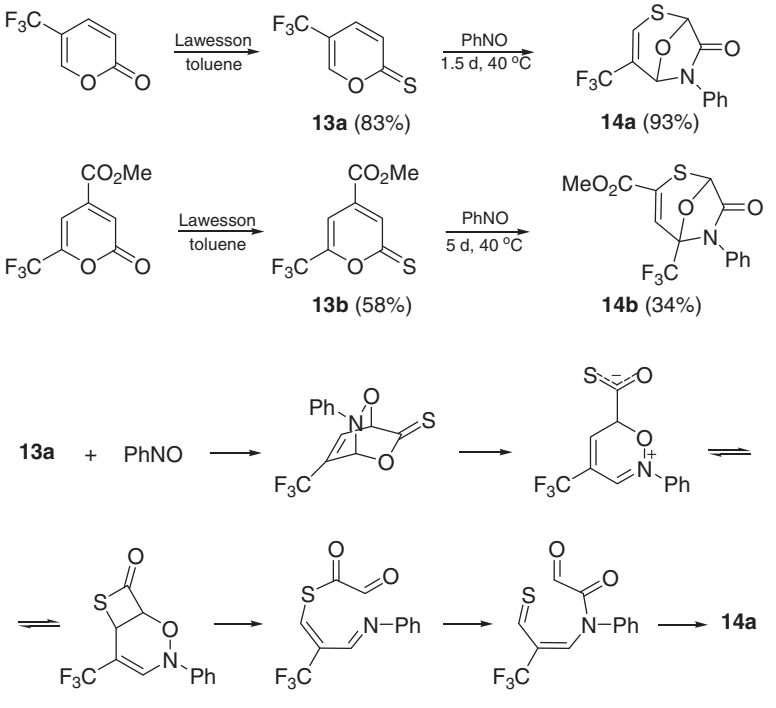
Scheme 2. Synthesis of 4-thiopyrones **8** and **9**.

The addition of sodium hydrogensulfide hydrate to the diynone **10** under basic conditions gave 4*H*-thiopyran-4-one **11** in almost quantitative yield. Peracetic acid oxidation converted thiopyrone **11** to the corresponding sulfone **12** (*10*) (Scheme 3).



Scheme 3. Synthesis of 4-thiopyrones **11** and **12**.

The trifluoromethylated 2*H*-pyran-2-thiones **13a**, **b** were prepared by reacting the corresponding 2*H*-pyran-2-ones in boiling toluene with Lawesson's reagent in 83% and 58% yields, respectively. Their reaction with nitrosobenzene led surprisingly to adducts **14a**, **b** which proved to be isomeric with the initially expected primary Diels–Alder cycloadducts. A plausible mechanism for the formation of compounds **14** was proposed (*11*) (Scheme 4).



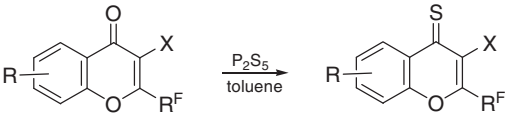
Scheme 4. Reactions of 2*H*-pyran-2-thiones **13a**, **b** with nitrosobenzene and a plausible mechanism for the formation of compound **14a**.

3. Sulfur analogs of fluorinated chromones

3.1. *Synthesis of fluorinated thio- and thionechromones*

We found that refluxing of 2-(polyfluoroalkyl)chromones **15** with P_2S_5 in toluene for 4 h affords 2-(polyfluoroalkyl)thionechromones **16** in moderate to high yields. Compounds **16** are crystals

colored from green to violet. The presence of a halogen atom in the 3-position does not prevent the reaction (*12*) (Scheme 5).

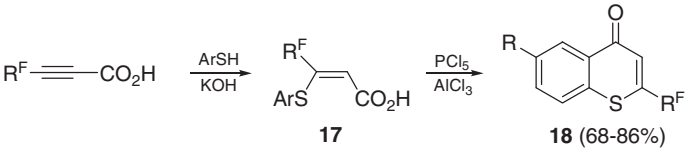


15 **16** (49-93%)

R^F = CF_3, $(CF_2)_2H$; R = H, Me, MeO; X = H, Cl, Br

Scheme 5. Synthesis of 2-(polyfluoroalkyl)thionechromones **16**.

Tamura et al. reported that due to the high nucleophilicity of arenethiols, the reaction involving arenethiols and polyfluoroalk-2-ynoic acids could be successfully carried out in aqueous ethanol in the presence of KOH at room temperature in 0.5 h. The resulting arylthioacrylic acids **17** have the *Z*-configuration of the double bond; on successive treatment with PCl_5 and $AlCl_3$ in benzene at room temperature, they produce 2-(polyfluoroalkyl)thiochromones **18** in high yields (*13*) (Scheme 6).

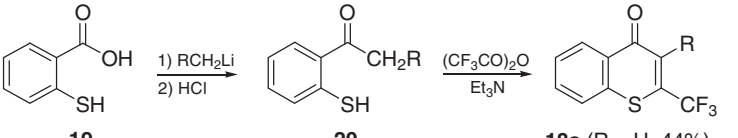


17 **18** (68-86%)

R^F = CF_2H, CF_3, $(CF_2)_3H$; R = H, Me, MeO, Cl

Scheme 6. Synthesis of 2-(polyfluoroalkyl)thiochromones **18**.

The modified Baker-Venkataraman reaction of alkyl 2-mercaptophenyl ketones **20**, prepared from thiosalicylic acid **19** and the corresponding alkyllithium, with trifluoroacetic anhydride in the presence of triethylamine in boiling THF, gave 2-(trifluoromethyl)thiochromones **18a**, **b** (*14*) (Scheme 7).



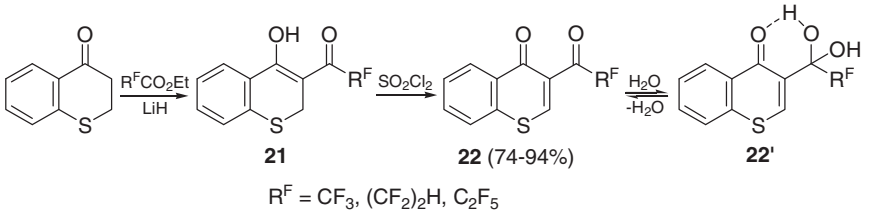
19 **20**

18a (R = H, 44%)
18b (R = Pr, 23%)

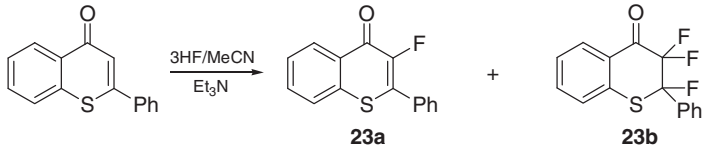
Scheme 7. Synthesis of 2-(trifluoromethyl)thiochromones **18a**, **b**.

3-(Polyfluoroacyl)thiochromones **22** were prepared in high yield via a chlorination–dehydrochlorination sequence by treating 3-(polyfluoroacyl)-4*H*-thiochroman-4-ones **21** with sulfuryl chloride (*15*). Like 3-(polyfluoroacyl)chromones (*16*, *17*), these compounds exist as a mixture of the nonhydrate form **22** and the hydrate **22'** (3:2 for $R^F = CF_3$ in $CDCl_3$ and DMSO-d_6) (Scheme 8).

By anodic fluorination of thioflavone, 3-fluorothioflavone (**23a**, 22%) and 2,3,3-trifluorothioflavanone (**23b**, 42%) have been synthesized (*18*, *19*) (Scheme 9).

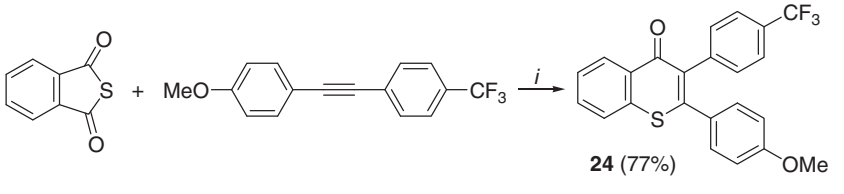


Scheme 8. Synthesis of 3-(polyfluoroacyl)thiochromones **22**.



Scheme 9. Synthesis of 3-fluorothioflavone (**23a**).

Nickel-catalyzed cycloadditions have been developed where thiophthalic anhydride reacts with alkynes to afford isothiocoumarins, benzothiophenes and thiochromones depending on the reaction conditions. Selective formation of thiochromone **24** was observed in benzene at 130°C in the presence of Ni(0)/PMe_3 (*20*) (Scheme 10).

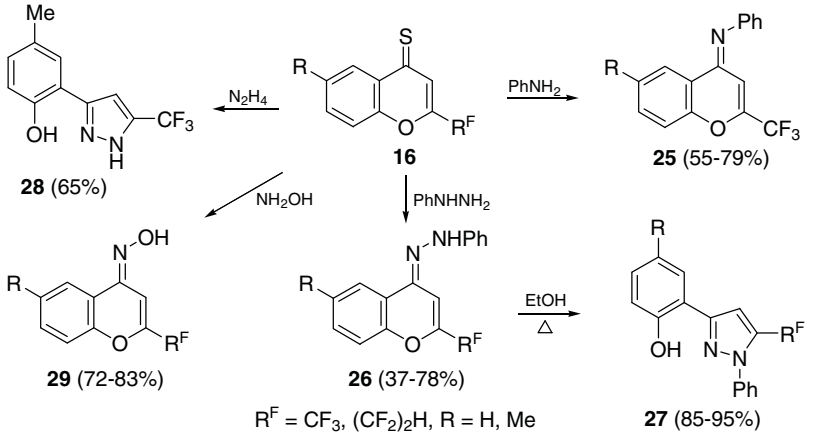


Scheme 10. Synthesis of thiochromone **24**. Reaction conditions: (i) Ni(0)/PMe_3, benzene, 130°C, 5 h.

3.2. *Reactions of fluorinated thio- and thionechromones*

On refluxing in butanol for 4 h, thionechromones **16** react with aniline at the C-4 atom to give anils **25** in good yields (Scheme 11). When these compounds are refluxed in ethanol in the presence of concentrated HCl, they hydrolyze to 2-(polyfluoroalkyl)chromones **15**, whereas in aqueous AcOH the reaction ceases at intermediate 2-hydroxy-2-(trifluoromethyl)chroman-4-ones. The reactions of aliphatic primary amines (benzylamine and 2-aminoethanol) with **16** occur ambiguously and afford a complicated mixture of substances (*12*). This fact is in contrast to the behavior of 2-R^F-chromones **15**, whose reaction with primary amines at C-2 with the formation of 3-amino-1-(2-hydroxyaryl)prop-2-en-1-ones is one of the most characteristic (*21*).

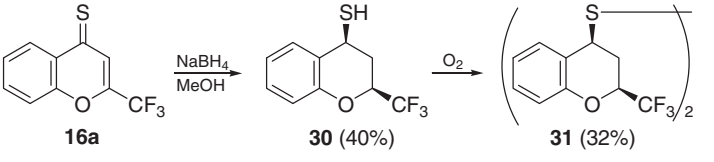
Thionechromones **16** react with phenylhydrazine readily at room temperature (*12*). The reaction is accompanied by vigorous H_2S evolution and affords within several minutes phenylhydrazones **26**, whose non-fluorinated analogs were synthesized earlier under more drastic conditions (*22*, *23*). On boiling in ethanol in the presence of concentrated HCl, phenylhydrazones **26** undergo ring closure to previously known 5-R^F-pyrazoles **27** (*24*). The reaction with hydrazine hydrate occurs as easily as that of 2-R^F-chromones **15** and affords pyrazole **28**, whereas a similar reaction with



Scheme 11. Reactions of thionechromones **16** with N-nucleophiles.

hydroxylamine (ethanol, ~20°C, 5 min) proceeds at the thione group to give chromone oximes **29** in high yields (*12*) (Scheme 11).

The reduction of 2-(trifluoromethyl)-4*H*-chromene-4-thione **16a** is impeded by the oxidative dimerization of the intermediate thiol, which affords a mixture of *cis*-2-(trifluoromethyl)chromane-4-thiol **30** and bis(2-trifluoromethylchroman-4-yl) disulfide **31**, which were separated by simple recrystallization from hexane. Interestingly, disulfide **31** was the single product that was isolated in 23% yield from the reaction of 3-chloro-2-(trifluoromethyl)-4*H*-chromene-4-thione (**16**, $R^F = CF_3$, X = Cl, R = H) with sodium borohydride (*25*) (Scheme 12).

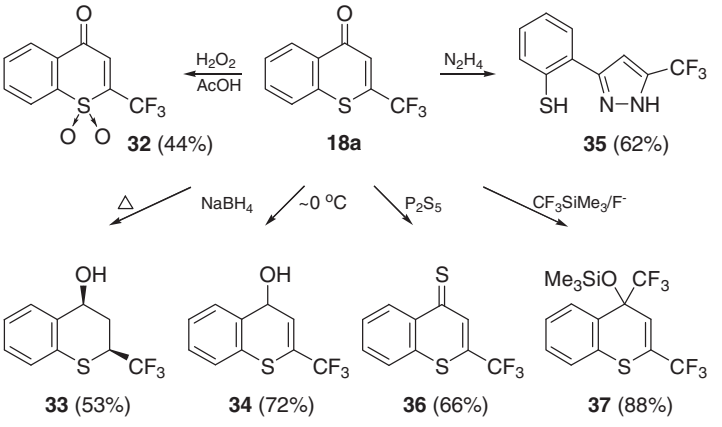


Scheme 12. Reduction of 2-(trifluoromethyl)-4*H*-chromene-4-thione **16a**.

Thiochromone **18a** is oxidized on heating with H_2O_2 in glacial acetic acid to give sulfone **32**; when refluxed with excess $NaBH_4$ in propan-2-ol, thiochromone **18a** is reduced to *cis*-2-(trifluoromethyl)thiochroman-4-ol **33**. Reduction of **18a** under milder conditions (~0°C) with a little excess of $NaBH_4$ can be stopped at the step of 2-(trifluoromethyl)-4*H*-thiochromen-4-ol **34**. Treatment of **18a** with hydrazine hydrate at room temperature gave pyrazole **35**; when refluxed with P_2S_5 in toluene for 1 h, it afforded 2-CF_3-dithiochromone **36** (*26*) (Scheme 13).

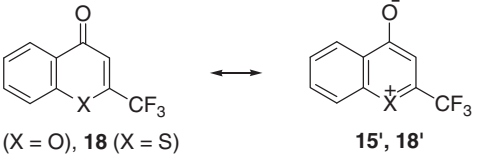
It was surprisingly found that thiochromone **18a** reacted with Ruppert's reagent to give as a sole product 2,4-bis(trifluoromethyl)-4*H*-thiochromen-4-yl trimethylsilyl ether **37** in 88% isolated yield after water hydrolysis (*27*). This result indicated that the reaction of **18a** took an entirely different course when compared with reactions of CF_3SiMe_3 with 2-R^F-chromones **15**, which react at C-2 (*20*), and exclusively proceeded as a nucleophilic 1,2-addition (Scheme 13).

The observed striking differences in reactivity between 2-CF_3-chromones **15** and 2-CF_3-thiochromones **18** appear to be connected with the difficulty met by the nucleophile in cleaving the thiopyrone S–C bond arising from the less electronegative character of the sulfur atom, which strongly reduces the electrophilicity of the 2-position, and the greater aromaticity of the thiochromone system as compared with chromones (structures **15'** and **18'**, Scheme 14).



Scheme 13. Reactions of thiochromone **18a**.

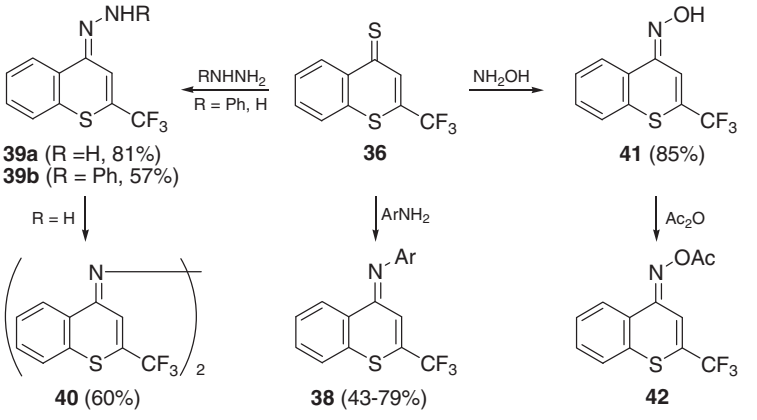
In fact, there is some double-bond character to S1–C2 (1.712 Å) and C3–C4 (1.457 Å) in 3-formylthiochromone (*28*), indicating a significant contribution of the resonance form **18'** involving the delocalization of the lone pair on sulfur into the carbonyl (for thiophene S1–C2 (1.712 Å)) (*29*). This delocalization is also reflected in the IR spectra of thiochromones, which have a carbonyl band at 1610–1630 cm^{-1}, that is, considerably lower than those of chromones (1650–1670 cm^{-1}).



Scheme 14. Resonance structures of chromone **15** and thiochromone **18**.

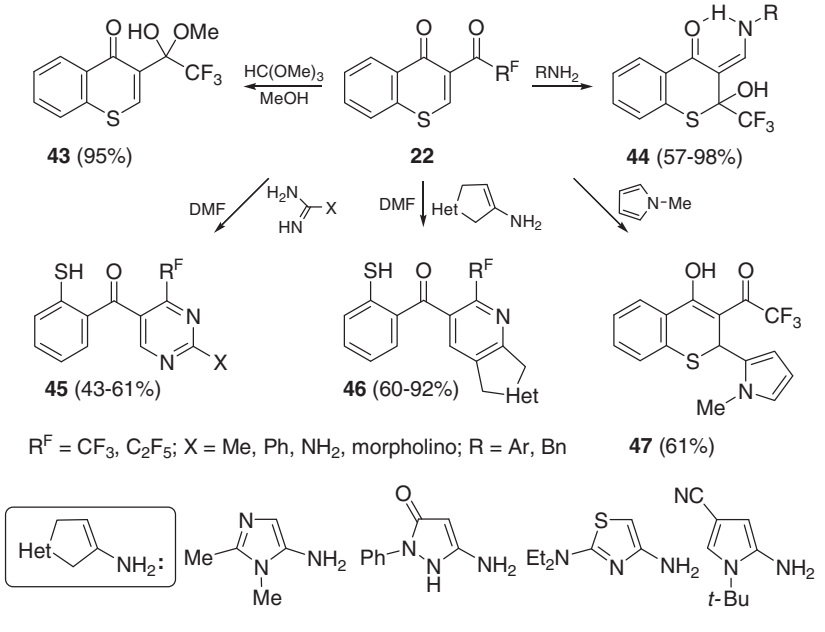
Full sulfur analogs of chromones (4*H*-thiochromene-4-thiones or dithiochromones) are poorly studied. It is only known that dithioflavones react with primary aliphatic amines to give thiochromenimines (*30*), while unsubstituted dithiochromone isomerizes into dithiocoumarin on heating with P_2S_5 (*31*). We found that 2-(trifluoromethyl)dithiochromone **36** also reacts with aniline, *p*-anisidine, and α-naphthylamine in boiling butanol at the thione group to give anils **38** in good yields. Treatment of dithiochromone **36** with hydrazine hydrate and phenylhydrazine gave hydrazones **39a**, **b** and azine **40**, whereas with hydroxylamine **36** reacted as easily as did thionechromones **16**, giving oxime **41**. When treated with acetic anhydride in the presence of catalytic amounts of concentrated H_2SO_4, oxime **41** underwent O-acetylation into compound **42** (*26*) (Scheme 15).

All these reactions proceed by nucleophilic 1,2-addition to give the corresponding derivatives of 2-(trifluoromethyl)thiochromone **18a** without opening of the thiopyrone ring. Attempts to obtain five- and six-membered heterocycles from dithiochromone **36** and dinucleophiles, such as hydroxylamine, hydrazines and amidines under the same conditions that had previously been used for the corresponding reactions of 2-(trifluoromethyl)chromones **15**, failed (*26*). Thus, despite the presence of the electron-withdrawing CF_3 group at the C-2 atom, thione-, thio- and dithiochromones **16**, **18** and **36** react with nucleophilic agents mainly at the C-4 atom, in sharp contrast to 2-R^F-chromones **15**, whose most characteristic reactions occur at C-2 and are followed by opening of the pyrone ring (*21*).



Scheme 15. Reactions of dithiochromone **36** with N-nucleophiles.

Although 3-R^FCO-thiochromones **22** are less reactive than 3-R^FCO-chromones (*16*, *17*), they are still able to react with methyl orthoformate (methanol, HCl), amines (benzene, reflux, 5 h), and amidine and guanidine salts (DMF, 100°C, 12 h) to give good yields of the corresponding hemiketal **43**, thiochromanones **44** (*32*) and pyrimidines **45** (*33*), respectively. Iaroshenko et al. reported that 3-R^FCO-thiochromones **22** react with heterocyclic amines as reported previously for the 3-R^FCO-chromones (*34*). In contrast to the case of 3-R^FCO-chromones, reaction of **22** with hetarylamines proceeded under harsher conditions (DMF, 110°C, 54–84 h) and appeared to be more regioselective, giving the set of diverse heteroannulated pyridines **46** bearing the R^F substituent at the α-position of the pyridine core as the sole isolated products in high yields (*32*). A somewhat unexpected result was obtained from the reaction of **22** ($R^F = CF_3$) with *N*-methylpyrrole. In this case, the reaction proceeded without cleavage of the thiopyrone ring to give the pyrrolyl derivative **47** in 61% yield (*32*) (Scheme 16).

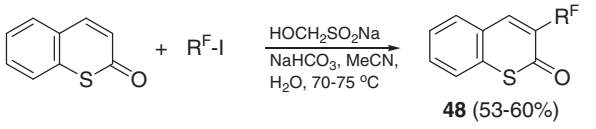


Scheme 16. Reactions of 3-(polyfluoroacyl)thiochromones **22**.

Thus, unlike 2-(trifluoromethyl)thiochromones **18** and **36**, the reactions of 3-(trifluoroacetyl) thiochromones **22** with primary amines, amidines and hetarylamines proceed as 1,4-nucleophilic addition with subsequent opening of the thiopyrone ring and cyclization with the participation of the CF_3CO group to give the corresponding heterocyclic products in good yields.

4. Sulfur analogs of fluorinated coumarins and isocoumarins

Huang et al. (*35*) reported that thiocoumarin reacts with perfluoroalkyl iodides in the presence of sodium hydroxymethanesulfinate (Rongalite) to give the corresponding 3-(perfluoroalkyl)thiocoumarins **48** selectively and under mild conditions. A free-radical mechanism was proposed for the reaction (Scheme 17).

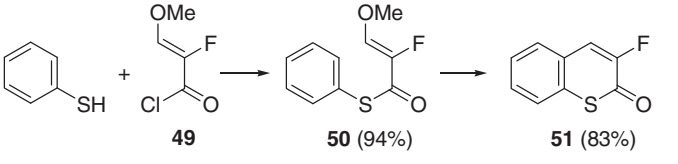


48 (53-60%)

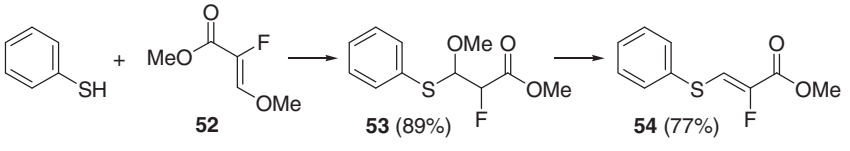
$R^F = F(CF_2)_6$, $Cl(CF_2)_4$, $Cl(CF_2)_6$

Scheme 17. Synthesis of 3-(perfluoroalkyl)thiocoumarins **48**.

The reaction of (*Z*)-2-fluoro-3-methoxyprop-2-enoyl chloride **49** with thiophenol in pyridine and diethyl ether at room temperature gave compound **50**, which was converted into 3-fluorothiocoumarin **51** under the action of concentrated sulfuric acid in chloroform at 60°C for 1 h (*36*) (Scheme 18).



49 **50** (94%) **51** (83%)



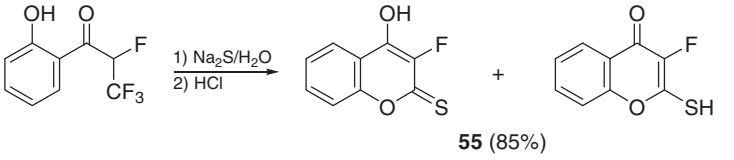
52 **53** (89%) **54** (77%)

Scheme 18. Synthesis of 3-fluorothiocoumarin **51**.

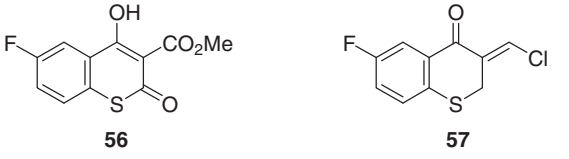
A different mode of interaction was observed with the ester **52**. In this case, the thiophenol underwent a 1,4-addition giving rise to the monothioacetal **53**. When this compound was heated in the presence of potassium hydrogen sulfate to 150°C, methanol was eliminated and methyl 2-fluoro-3-(phenylthio)acrylate **54** formed (*36*) (Scheme 18).

Dmowski (*37*) reported facile preparation of some new pyrone ring monofluorinated chromones and coumarins, including sulfur containing derivatives, by treatment of *o*-hydroxy-2,3,3,3-tetrafluoropropiophenone with amines and sodium sulfide. In the latter case, 3-fluoro-4-hydroxy-2-thionecoumarin **55** as a mixture of two tautomers was obtained (Scheme 19).

The methyl ester of 6-fluoro-4-hydroxy-2-oxo-2*H*-thiochromene-3-carboxylic acid **56** was used as the starting material for the preparation of bioactive compounds capable of decreasing HIF hydroxylase enzyme activity, thereby increasing the stability and activity of hypoxia



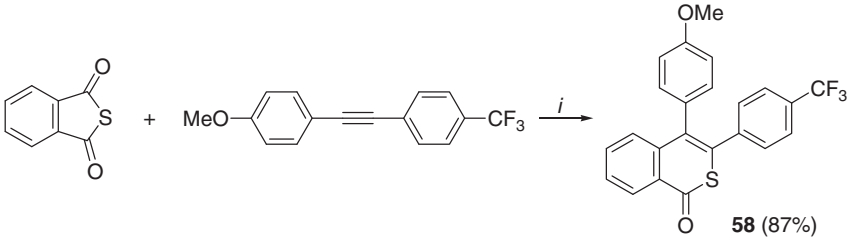
Scheme 19. Reaction of *o*-hydroxy-2,3,3,3-tetrafluoropropiophenone with sodium sulfide.



Scheme 20. Structures of compounds **56** and **57**.

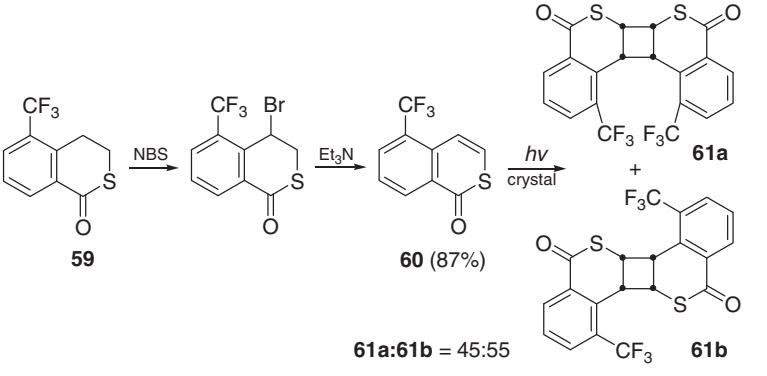
inducible factor (HIF) (*38*). Compound **57** was suggested as an example of a novel antibacterial and anticancer agent (*39*) (Scheme 20).

1*H*-2-Benzothiopyran-1-one (isothiocoumarin **58**) was prepared from thiophthalic anhydride and the corresponding tolan in the presence of Ni(0)/PPr_3 catalyst in combination with Lewis acid (MAD: methylaluminum bis(2,6-di-*tert*-butyl-4-methylphenoxide) (*20*) (Scheme 21).



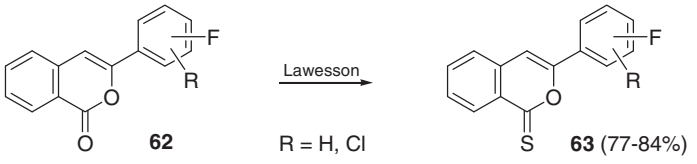
Scheme 21. Synthesis of isothiocoumarin 58. Reaction conditions: (i) Ni(0)/PPr_3, MAD, toluene, 130°C, 3 h.

The synthetic approach to 5-(trifluoromethyl)isothiocoumarin **60** involves a bromination/dehydrobromination sequence that proceeds via thiopyranone **59** and the intermediate 4-bromoisothiochromanone as shown in Scheme 22. Irradiation (350 nm) of **60** as homogeneous solid film affords a 4:5 mixture of dimers **61a** and **61b** which were not separated (*40*) (Scheme 22).



Scheme 22. Synthesis and irradiation of 5-(trifluoromethyl)isothiocoumarin **60**.

Isothionecoumarins **63** were synthesized in high yields by thionation of isocoumarins **62** by refluxing with Lawesson's reagent in toluene for 3 h and their anticancer and antimetastatic evaluation was described (*41*). Alternatively, a rapid microwave-accelerated thionation of some 3-substitued isocoumarins **62** to the corresponding isothionecoumarins **63** was achieved employing Lawesson's reagent under solventless conditions (*42*) (Scheme 23).



Scheme 23. Synthesis of isothionecoumarins **63**.

5. Conclusion

Analysis of the published data demonstrates that of the diverse fluorine-containing six-membered sulfur heterocycles, thiochromone derivatives have now been studied most comprehensively. Data on fluorinated thiopyrones and coumarins are quite scarce.

Despite the ready accessibility of trifluoromethylated thiochromones, these compounds have long remained out of sight of chemists engaged in synthesis, and their systematic study has started only in recent years. Nevertheless, it is already clear that some of them, for example, 3-(trifluoroacetyl)thiochromones, are valuable substrates for the synthesis of diverse partially fluorinated heterocycles with potential biological activity. The diversity of properties of these compounds is due to the fact that, being actually highly reactive geminally activated alkenes with a good leaving group at the β-carbon atom, they acquire the ability to undergo additional reactions related to opening and transformation of the γ-thiopyrone ring. These reactions have been used to prepare various R^F-containing fused pyridines and pyrimidines.

In view of the fact that 20–30% of modern pharmaceuticals and 30–40% of agrochemical preparations contain at least one fluorine atom in the molecule (*43*), the research dealing with modification and study of the reactivity of fluorinated sulfur-containing heterocycles aimed at extending the synthetic scope of these compounds appear to be a topical and promising line for the future research into fluorine-containing heterocyclic compounds and search for new biologically active substances.

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